New additive technology provides scratch resistance

Increasing use of a wide variety of polypropylene compounds in the automotive industry has prompted the need for a new additive to impart long term scratch resistance. Kathrin Lehmann and Philipp Tomuschat of Evonik Goldschmidt GmbH explain.

There are a number of plastic applications that benefit from scratch resistance regardless of the polymer used. For example, arm chairs and certain parts of furniture, any kind of consumer goods with daily use, computer parts and in particular automotive applications. Today's consumer expects a product to look new even after a period of use. A laptop case or a dashboard with a number of visible scratches does not fulfil this expectation and is perceived as a product with reduced value. In contrast products with no visible damage after use support the quality image of a product/ brand and encourage the customer to stick with products from a manufacturer when it comes to a new purchasing decision. In order to guarantee an undamaged surface for the lifetime of a product high value polymers like polyamide (PA) or styrene-based polymers (ABS, SAN) can be used or the mechanical properties of standard polymers like polypropylene (PP) can be increased by fillers and additives. This article summarizes the technical status of scratch resistant PP compounds in the automotive industry with a focus on the applications, measurement of scratch resistance, different additive technologies available and additional parameters affecting antiscratch performance.

Automotive

A great many polymers — PA, ABS (acrylnitrile-butadiene-styrene), PC (polycarbonate)/ABS, PA/PP, TPU (thermoplastic urethanes) among others — are used in the car and truck industry. However, because of ongoing cost savings in the automotive industry the importance of talc filled PP and PP/TPO (thermoplastic polyolefins) systems continues to grow. Without further treatment, such as an antiscratch coating, the scratch resistance of these systems do not meet the requirements of the automotive industry.

From a cost perspective an additional coating step is affordable for high value cars only, although there is still a need for scratch resistance for medium and small sized cars also. Therefore, there is a need for novel additives in the industry creating inherent scratch resistance and eliminating the need for additional coatings.

Figure 1 shows a typical automotive application – door handles made from PP and from 20% glass fibre filled PA. In general, polyolefins are used for a variety of interior parts such as door panels, dashboards, centre consoles as well as exterior parts like bumpers.

For mechanical reasons automotive polyolefin compounds contain PP, talc and depending on the final application TPOs which can replace parts of the PP. Compounds with TPOs are particularly suitable for exterior parts because of increased mechanical flexibility. All components of the formulation such as polymer type, talc grade and even the pigment masterbatch influence the final scratch resistance of the moulded plastic part. For each end-use application, for example bumper or dashboard, a specific formulation is developed which is in general different for every car manufacturer or component supplier.

Figure 1: Door handles (interior and exterior).

As a result a large number of materials are used in automotive PP compounds, which means that antiscratch additives need to be compatible with a wide variety of these materials. Therefore, the ideal antiscratch additive for the automotive industry must not limit the choice of materials to adjust mechanical properties such as rigidity, elasticity, CLTE values (coefficient of linear thermal expansion), low temperature notched impact strength or indeed the price.

During the past few years plain plastic surfaces as a standard material in passenger compartments have been replaced by plastic parts with grained surfaces. Not only is the appearance more pleasant but the feel is dramatically improved also. Figure 2 shows typical grained surfaces of European and American car manufacturers that are widely used for interior automotive applications.

As well as the ingredients of a formulation, the nature of the surface has a significant impact on the scratch resistance. A smooth or plain surface is less susceptible to damage than a grained surface. For design reasons and the advantages mentioned grained surfaces are preferred by consumers and are expected to play an even more dominant role in the future. Because of the importance of grained surfaces and their sensitivity to scratch damage Evonik has concentrated its efforts

Figure 2: Typical grained automotive surfaces.

Figure 3: Erichson equipment to evaluate scratch and mar resistance.

in investigating the scratch resistance for automotive parts on this type of surface.
A typical polyolefin compound may have the following formulation for an interior application:

PP copolymer (+TPO)	48-78%
Pigment masterbatch	2-5%
Talc	15-40%
TEGOMER® AntiScratch 100	2-4%
Other additives	1%

(For example, antioxidants; UV stabilizer, calcium stearate)

Measurements

At present the automotive industry has various tests for the evaluation of scratch resistance. A number of tests and different equipment exist, such as the Erichson scratch tester, the Five Finger scratch tester and the PSA abrasion tester. The basic principle of all methods to determine the scratch resistance of a surface is the same. A defined mechanical stress is applied to the surface and the resulting damage is quantified. That means that the numbers obtained in the different tests are not comparable but the relative results for different materials are similar. These studies used the Erichson scratch tester which is shown in Figure 3.

The Erichson scratch tester allows the evaluation of scratch and mar resistance at forces between 5N and 20N. In the tests forces of 5N and 10N were applied at a speed of 1000 mm/min of the scratch tool. The tool is in contact with the surface through a round shaped tip with a diameter of 1mm. A pattern of 20 lines (10 in one direction and 10 at right angles to those) is generated by the tester and the scratch resistance is determined afterwards by measuring the difference in brightness of the scratched and the unscratched surface. Figure 4 illustrates the result that can be achieved by the Erichson equipment.

The difference in brightness is measured by a BYK Gardner instrument and the resulting delta L* value (CieLab system) is used as an indicator of the scratch resistance of the compounds.

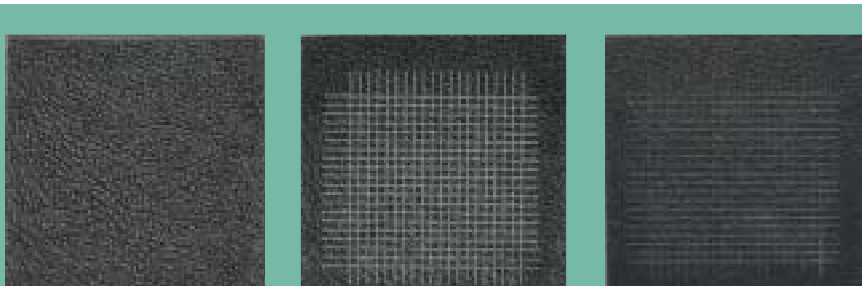

Figure 4: Unscratched surface (left), scratched without additive (centre) and scratched with additive (right).

Figure 5 shows the explanation for the reduced appearance of scratches using organic modified siloxanes (OMS) as well as the correlation between scratch depth and delta L* value. For the determination of the scratch depth a convocal laser scanning microscopy (CLSM) was used.
Due to the smoother surface of the compound with the OMS additive the applied force is not capable of creating the same depth of scratch. The deeper the scratch is, the more brightly particles of filler, such as talc particles, reflect the light. Therefore, the scratched surface is brighter than the unscratched surface and the delta L* value is higher. As shown in the central diagram of Figure 5 there is a good correlation between the scratch depth and the delta L* value.

This 40% talc filled PP compound, which is almost black, is one of the most complicated compositions compounders have to deal with. At a lower talc loading the scratch depth is less pronounced and the delta L* value is much lower.

Current technologies

When considering which additive technologies are suitable to improve a lack of scratch resistance, it must be concluded that a new additive has to guarantee two things. Firstly, there must be a significant improvement in scratch resistance immediately after the moulding process. Secondly, permanent scratch resistance is important not only during the manufacture of the car but even more so in use for the consumer.

Currently the automotive industry mainly uses additives selected from the chemical groups of amides, silicone oil or grafted polymers or mixtures of those offered as additive compounds. Table 1 summarizes the properties of PP compounds with antiscratch additives that can be achieved by the different technologies. The properties of a PP compound containing the newly designed organic modified siloxane TEGOMER® AntiScratch 100 is displayed in the first column of Table 1.

The new additive yields a permanent scratch resistance and no fogging or gloss change is observed because the additive does not migrate. In addition, it does not

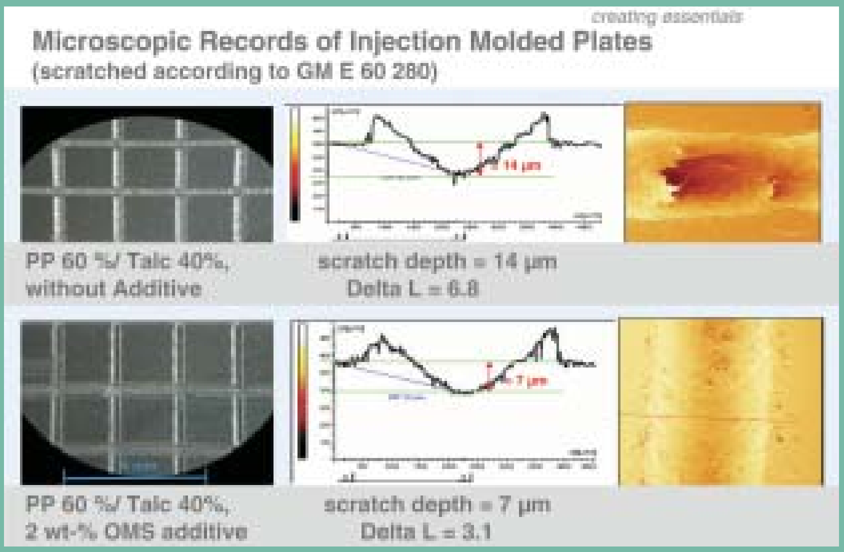

Figure 5: Scratch depth and delta L value without and with OMS additive.*

have any negative effect on the odour of the compound, which is particularly important to pass smell tests undertaken by car manufacturers.

Influence of talc

As discussed the filler loading plays an important role in scratch resistance. Figure 6 illustrates this point for a polypropylene/talc compound using different additive technologies in combination with a 3.0 micrometer talc with 12% and 20% loading.
These compounds are typical for interior applications, such as door panels or dashboards. TEGOMER® AntiScratch 100 protects surfaces against scratches significantly better than standard additives which are currently widely used in the industry.
Obviously scratch prevention gets more difficult with an increase of the applied force. Results obtained from a 5N force do not vary that much, however differences between compounds become more evident at a force of 10N. This is the reason why results at 10N Erichson are often used for an approval at car manufacturers. Accordingly, 10N is used for the appraisal of different ingredients when developing a novel formulation.

The grade of talc grade selected for reasons of gloss or to influence the mechanical properties of the compound is particularly important in affecting the final scratch resistance. The d50 and top cut values of the talc are typical characteristics that allow the compounder to adjust the final properties of the compound to meet the needs of a particular automotive application. Figure 7 and Figure 8 show the resulting 10N delta L* values in a copolymer formulation with 18% talc filling.
The comparison of the different surfaces K 31 and K 09 also demonstrates the influence of designer choice as a parameter. However, the use of TEGOMER® AntiScratch 100 has demonstrated a good increase in scratch resistance that is independent of how the initial formulation performed without the additive.

Long term resistance

Immediate scratch resistance or in particular after 24 hours is highly relevant during car manufacture on the production line. Even more important is the long term or permanent scratch resistance of the moulded part for the end user. This is usually tested through an ageing test by subjecting the material to a temperature of 70-80°C for one week.
Figure 9 illustrates the ageing behaviour of different additive technologies.

Table 1: Additive technologies used for prevention of scratch resistances

	TEGOMER® AntiScratch 100	Amides	Silicon oil masterbatches	Grafted polymers
Scratch 1day/RT	++	++	++	(+)
Scratch 7days/80°C	++	0	(+)	(+)
Migration	No	Strong	Yes	Partly
Paintability	Possible	Limited	Often not possible	Limited
Odour	No	Yes	No	Partly
Notched Impact	+	0	0	0
Use during compounding	+	+	+	+
Use in moulding operations	++	0	-	0 or –
Addition level (%)	2-4	0.5-2.0	2-4	>3

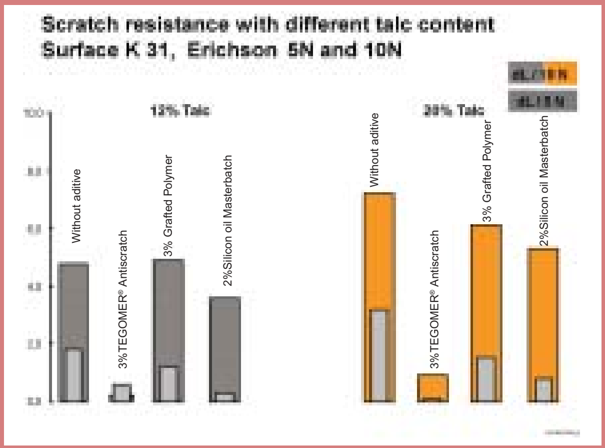

Figure 6: Scratch resistance depending on talc loading and additive technology.

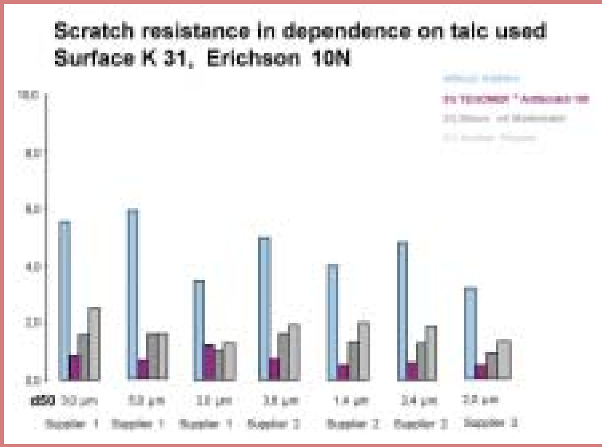

Figure 7: Different talc grades in a 18% talc filled copolymer, surface K 31.

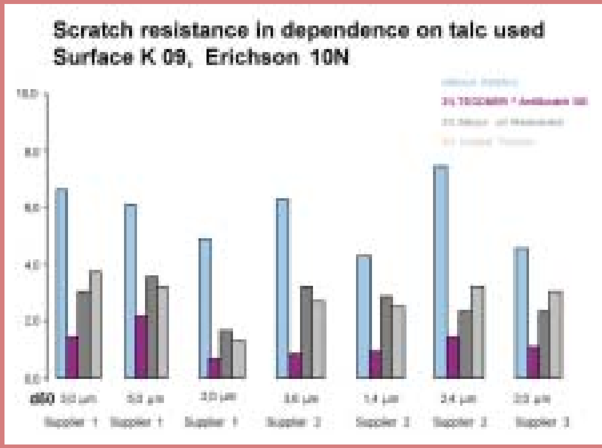

Figure 8: Different talc grades in a 18% talc filled copolymer, surface K 09.

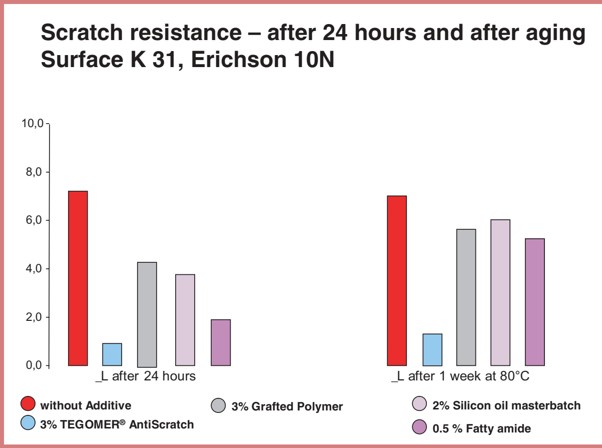

Figure 9: Permanent scratch resistance depending on the additive technology used.

The lowering of scratch resistance shown by the increase of delta L* values after ageing can be explained by the migration of the different additives to the surface. In particular the low molecular amides yield poor results. Moreover, they are undesirable because of their effect on the odour of a compound. Silicone oil and grafted polymers, which are often combined with amides, show a significant increase of delta L* values, too. This increase of delta L* and corresponding loss of scratch resistance can be attributed to this migration behaviour. The migration of material is not only disliked for this effect but also because it influences the final appearance of the surface in regard to the gloss.

If such substances are used in compounds that are ultimately secured by an adhesive as automotive parts then undesirable side effects may occur. In addition, the paintability required for high-end applications is not possible on surfaces contaminated with silicone oil or the interlayer adhesion of the coating and plastic part will be damaged creating peal-off effects.

There can often be problems when combining antiscratch additives with other ingredients of the compound, for example odour absorbers. Sometimes they have to be used to reduce the smell that can be created from pigments in the masterbatch or the polyolefin itself. TEGOMER® AntiScratch 100 can be easily combined with the odour absorber TEGOSORB® P.Y. 88 without reducing the antiscratch performance.

Conclusions

The dependence of scratch resistance on a number of different parameters has driven the development of a novel additive for automotive polyolefin compounds. TEGOMER® AntiScratch 100 is an additive for PP compounds that can overcome problems caused by different grained surfaces, various talc grades or different loading levels. The new technology is migration-free and allows permanent scratch resistance for the automotive industry.

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